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TITLE: Selective hydrogenation of diene(s) and/or acetylene(s) - in hydrocarbon fractions,
under specified conditions using a catalyst contg. nickel and platinum-gp. metal

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BASIC-ABSTRACT:

The selective hydrogenation of diolefins and/or acetylenes in hydrocarbon fractions is effected at 0-250 (pref. 30-180 degrees) C., 7-100 (20-70) bars, an LHSV of 0.2-5 (0.5-3), an H2 rate of 70-360 (70-150) m3/m3 and an H3 consumption of 5-100 (10-90) m3/m3, using a catalyst comprising 1-50 wt.% Ni on a support and 1-50 ppm of a Pt-gp. metal.

Used, e.g. in treating 3-4 C fractions or 15-225 degrees C boiling gasoline fractions, and esp. gasoline reduced by thermal cracking at >593 degrees C in the presence of diluent steam and/or inert heat transfer agents. The addn. of the modifying Pt-gp. metal results in an improved reducibility of the Ni catalyst and enables the reduction to take place over a wider temp. range than hitherto.

TITLE- SELECT HYDROGENATION DIENE ACETYLENE HYDROCARBON FRACTION
TERMS: SPECIFIED CONDITION CATALYST CONTAIN NICKEL PLATINUM GROUP
METAL

DERWENT-CLASS: E17 H04

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(54) IMPROVEMENTS RELATING TO SELECTIVE HYDROGENATION

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, EC2Y 9BU, a British Company, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:-

5 This invention relates to a process for the selective hydrogenation of di-olefins and/or acetylenes in the presence of mono-olefins utilising a modified supported nickel catalyst. The catalytic selective hydrogenation of di-olefins and/or acetylenes in unsaturated hydrocarbon fractions containing them and also mono-olefins is a well established process. The hydrocarbon fractions may be C₃ and/or C₄ fractions or gasoline fractions boiling in the range 15 to 225°C. Because of the gum-forming characteristics of these highly unsaturated materials the process is carried out at temperatures below 250°C in the liquid phase. Aromatics, if present, remain unhydrogenated as do at least a proportion of the mono-olefins, these being hydrogenated, if necessary, in a second higher temperature stage. A particularly suitable catalyst is a supported, predominantly elemental, nickel catalyst, the use of such a catalyst being described and claimed in UK Patent No. 848232. Other patents describing improvements or modifications to the process are UK Patent Nos. 899652, 972245 and 1301477.

10 The process is particularly suitable for gasoline produced by thermal cracking above 593°C, in the presence of diluent steam and/or an inert heat transfer agent such as sand. Such thermal cracking processes are designed primarily for the production of light olefins e.g., ethylene and propylene, the gasoline produced being a by-product.

15 C₃ and/or C₄ fractions from the steam cracking may also be selectively hydrogenated to remove dienes or acetylenes depending on the use to which these fractions are to be put.

20 The presence of highly unsaturated gum-forming hydrocarbons leads to the gradual deposition of polymeric material on the catalyst and eventually to a high pressure drop across the reactor. To increase the catalyst life, treatment with hydrogen, as described and claimed in UK Patent No. 907348, has been used. The combination of reactivation, careful control of the hydrogenation to minimise gum formation, and the relative cheapness of the catalyst has, up till now, made it unnecessary to consider catalyst regeneration on a commercial scale.

25 However, the increasing cost of nickel has increased the cost of the catalyst. Further, the severity of steam cracking has been steadily increasing giving more highly unsaturated gasolines and a consequent shortening of the overall catalyst life. Regeneration of the catalyst has, in fact, already been proposed as a solution.

30 Our British Patent Specification No. 1455030 (BP Case 3711) discloses a process for regenerating a supported nickel catalyst which has been used for the selective hydrogenation of di-olefins and/or acetylenes in the presence of mono-olefins which comprises the steps of purging the catalyst of volatile hydrocarbon material with an inert gas at a temperature of from 120 to 350°C, burning off hydrocarbonaceous deposits with an oxygen/inert gas mixture at a temperature of from 350 to 450°C, initiating the reduction of

the oxidised catalyst with an hydrogen-inert gas mixture at 350 - 450°C and completing the reduction with hydrogen at 350 - 450°C.

The optimum temperature range for the reduction procedure is 390°C to 430°C.

At temperatures below 390°C, and more particularly below 350°C, the catalyst is not reactivated to its full potential. At temperatures above 430°C and more particularly above 450°C, the nickel is reduced to the form of relatively large crystallites of diminished activity.

In practice, control of the relatively narrow temperature range necessary for optimum reduction can be difficult to achieve.

We have now discovered that the addition of a modifying quantity of a platinum group metal to the nickel catalyst results in improved reducibility of the nickel catalyst and enables satisfactory reduction to take place over a wider range than hitherto.

Thus according to the present invention there is provided a process for the selective hydrogenation of di-olefins and/or acetylenes in a hydrocarbon fraction which process comprises contacting the hydrocarbon fraction in the presence of a supported nickel catalyst comprising in addition 1-50 ppm by weight of a platinum group metal at a temperature in the range 0° - 250°C, a pressure in the range 7-100 bars gauge, a liquid hourly space velocity in the range 0.2-5 v/v/hr, a hydrogen treatment rate of 70 - 360 m³/m³ and a hydrogen consumption rate of 5-100 m³/m³ a supported nickel catalyst comprising in addition from 1 - 50 ppm by weight of a platinum group metal.

The catalyst may contain from 1 to 50% wt of nickel, preferably 5 to 30% wt, by weight of total catalyst. The support may be any support stable up to 450°C, particularly one having a low activity for cracking and polymerising reactions. It may be a refractory oxide or other refractory compound of a Group II, III or IV element for example alumina, silica, or preferably, sepiolite.

The nickel catalyst may be prepared by impregnating the support with a solution of a complex of ammonia with a substantially water-insoluble nickel salt of an aliphatic monocarboxylic acid followed by reduction of the complex to elemental nickel to activate the catalyst.

The platinum group metal may be added in the form of an aqueous solution together with the nickel salt or in a subsequent second impregnation stage.

The platinum group metals are ruthenium, rhodium, palladium, osmium, iridium and platinum, with palladium being particularly preferred. Suitable salts of these metals include palladium chloride.

Although the nickel of the catalyst is predominantly present as elemental nickel during the selective hydrogenation, the selectivity is conferred by a partial sulphiding of the nickel, the sulphur:nickel atomic ratio being normally in the range 0.01 - 0.4:1, more particularly 0.01 - 0.2:1. The sulphur may be added by reaction with thiophene normally present in the feedstock or by presulphiding with a thiophene, thiacyclo-alkane having at least 4 carbon atoms in the ring, or dialkyl monosulphide at a temperature below 250°C. The aforementioned sulphur compounds may also be added to the feedstock to accelerate the partial sulphiding during the early stages of the selective hydrogenation.

The preferred feedstocks are gasoline fractions boiling in the range 15 to 225°C having the following characteristics:

45	Di-olefin content	% wt	4- 35, preferably 5-15	45
	Mono-olefin content	% wt	1- 20, preferably 1-10	
	Aromatic content	% wt	30- 85, preferably 45-75	
	Diene content	% wt	5- 30, preferably 10-15	
	Bromine number		10-100, preferably 30-80	
50	Total sulphur content	% wt	0.005-1.5, preferably 0.005-0.4	50
	Mercaptan sulphur	ppm wt	1-300, preferably 1-30	

The di-olefin, mono-olefin and aromatic contents may be determined by chromatography. The diene value is measured by UOP Test Method No. 326 - 65.

The preferred ranges above are those likely to be found in steam cracked gasolines produced by high severity steam cracking (i.e., cracking to product ethylene yields of 20 - 40% wt on feed). As previously indicated these highly unsaturated gasolines are particularly liable to deposit gum and polymer on the catalyst.

The selective hydrogenation process is a relatively low temperature process which is operated under the following conditions.

60	Temperature	°C	0-250, preferably 30-180	60
	Pressure	bars gauge	7-100, preferably 20-70	
	Space velocity	v/v/hr	0.2- 5, preferably 0.5-3	
65	Hydrogen treating rate	m ³ /m ³	70-360, preferably 70-150	65

Hydrogen consumption

 m^3/m^3

5-100, preferably 10-90

In initiating the regeneration the flow of feedstock is stopped but preferably the hydrogen flow is continued for 1 to 24 hours at the reaction conditions to purge the catalyst bed of feedstock. The need for regeneration may be seen from an increasing pressure drop of from 0.5 to 7 bars across the catalyst bed, by failure to maintain the desired hydrogen consumption by increasing the temperature, or by failure of known reactivation techniques to restore activity. Preferably regeneration is initiated when the pressure drop is still moderate, e.g., 0.5 to 2 bars, to reduce the amount of hydrocarbonaceous deposits required to be burnt off.

The regeneration may be preceded by specific techniques to reduce the amount of hydrocarbonaceous deposits on the catalyst, as will be discussed in more detail hereafter. In its simplest form the regeneration may be started by stopping the flow of feedstock and hydrogen and purging the catalyst with an inert gas, preferably steam, at 120 to 350°C. The pressure is preferably reduced to 1 - 10 bars gauge and the temperature may be gradually increased, e.g., at 50°C/hr to a maximum of 350°C. The inert gas flow rate may be from 100 - 2000 v/v/hr and the total purging time from 1 to 24 hours.

The burn off may be carried out at 300 to 500°C. The temperature is controlled by control of the oxygen content of the gas which may be from 0.2 - 5% mol. The inert gas used and the flow rate may be as for the purging, oxygen, preferably as air, being added to the purge gas. Preferably the burning is carried out in two or more stages.

Suitable stages may thus be:

Inlet gas at 350 - 370°C with a maximum bed temperature of 390 - 410°C.

Inlet gas at 390 - 410°C with a maximum bed temperature of 420 - 450°C.

The stages are considered to be complete when the oxygen content of the exit gas is the same as that of the inlet gas.

Preferably there is no recycle of the gas, this being unnecessary when using steam. If recycle is contemplated care should be taken to eliminate CO from the recycled gas.

At the completion of the burn off, the oxygen is shut off while maintaining the flow of inert gas. Preferably, the temperature of the inlet gas is reduced to 350 - 370°C.

It is believed that during the burn-off most, if not all, of the sulphur on the catalyst is oxidised to sulphate. Since reduction of nickel sulphate to nickel sulphide is highly exothermic an important feature of the present invention is the use of a hydrogen-inert gas mixture to initiate the reduction. The inert gas, preferably steam, helps to control the reduction and carry away the heat of reaction.

Preferably the initial gas contains from 15 to 85 mol % hydrogen the balance being inert gas. The hydrogen content is controlled to keep the temperature within the 300° - 450°C, preferably within the range 350 - 400°C. The total gas flow rate may be from 100 to 2000 v/v/hr and the overall time for this initial reduction from 1 to 10 hours.

Preferably the inert gas content of the gas is gradually reduced to zero within this time, while ensuring that the specified temperature is not exceeded. Suitably 20% reductions in inert gas flow are made hourly.

The final reduction is made with hydrogen alone at 150° - 450°C but preferably at 350 - 430°C. The hydrogen flow rate may be from 100 to 2000 v/v/hr and the time from 1 to 50 hours. Suitably the inlet hydrogen may be at 420 - 450°C with the maximum bed temperature at 410 - 430°C.

The catalyst may be cooled back to the normal operating temperature in a flow of hydrogen preparatory to recommencing the selective hydrogenation in standard manner.

The pressure during the various steps of the regeneration may be from 1 to 35 bars gauge, preferably 1 to 10 bars gauge. The term "inert gas" means a gas inert to the catalyst under the conditions of regeneration. It may, for example, be nitrogen but it is preferably steam. Since liquid water may harm nickel catalysts, the temperature of the regeneration should be such that no liquid water forms and care should be exercised in this respect. Preferably the gases used flow downwardly through the catalyst bed rather than upwardly.

As previously indicated, the quantity of hydrocarbonaceous deposits on the catalyst can be reduced, prior to the regeneration, by special techniques used singly or in combination.

The catalyst may be washed with a hydrocarbon liquid which may consist of or contain aromatics, naphthenes or paraffins. Preferably it contains at least 50% wt of aromatics. Preferably the liquid boils within the range 50 - 250°C and is substantially free of sulphur compounds. Suitable liquids include benzene, toluene, reformat, straight-run gasoline, or even steam cracker gasoline.

The wash liquid may be distilled to remove the dissolved polymer and recycled. The washing may be carried out under the following ranges of conditions.

Temperature*	°C	ambient - 300, preferably 50 - 250
Pressure	bars gauge	7 - 100, preferably 20 - 70
Space velocity	v/v/hr	**0 - 10, preferably 0 - 5
Hydrogen rate	m ³ /m ³	0 - 360, preferably 0 - 150

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The catalyst can also be treated with hydrogen under the following ranges of conditions.

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Temperature	°C	150 - 450, preferable 200 - 400
Pressure	bars gauge	7 - 100, preferably 20 - 70
Space velocity	v/v/hr	20 - 2000, preferably 100 - 1000

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* Selected so that the wash liquid remains substantially in the liquid phase.

** Corresponds to filling reactor under no-flow conditions, i.e., a static soak.

The invention is illustrated by the following examples.

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Example 1

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A nickel on sepiolite catalyst containing nominally 10 ppm wt palladium was prepared by adding 250 ml (186 grammes) of a standard Ni/sepiolite catalyst (containing 10% wt nickel) to a solution containing 0.001 grammes of PdCl₂ in 250 ml of deionised water. The catalyst was left in the solution for 24 hours at ambient temperature. Excess solution was then removed using a rotary evaporator. The catalyst was dried overnight at 120°C.

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Example 2

An evaluation of the reducibility of the Ni/sepiolite catalyst containing the trace of palladium was carried out on a small pilot plant. The reactor was packed with 50 ml (36.0 grammes) of the Pd doped Ni/sepiolite catalyst, which was reduced by heating the catalysts to 350°C for 4 hours under a once-through hydrogen flow of 50 litres/hour. Following reduction the catalyst was cooled back to and maintained at 80°C under hydrogen flow and then sulphided by passing over it n-heptane containing nominally 0.13% wt thiophene at 200 ml/hr, for 12 hours. The catalyst was then oxidised in a flow of nitrogen containing 1% oxygen at 450°C for 5 hours, after the unit had been purged of hydrogen.

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After oxidative regeneration of the catalyst, the unit was purged with nitrogen and then hydrogen and the catalyst was reduced successively at 250°, 300° and 350°C in flowing hydrogen at 50 litres/hour for 4 hours at each temperature. A sample of the catalyst was taken after each stage of reduction. To prevent oxidation of the reduced catalyst precautions were taken to avoid contact with the air. The catalyst was sampled under a nitrogen purge and samples were stored under water.

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The metallic nickel content of the catalyst samples were determined by treating the samples with hydrochloric acid and by measuring the volume of hydrogen evolved in a gas burette.

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The same procedure was repeated on 50 ml (34.3 grammes) of the standard nickel on sepiolite catalyst.

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Results

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Reduction Temperature	% Ni Reduced	
	Standard Ni/sepiolite	Pd/Ni/sepiolite
°C		
250	12	31
300	35	48
350	50	67

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This shows that following a simulated regeneration the catalyst containing the precious metal is more readily reduced.

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WHAT WE CLAIM IS:

1. A process for the selective hydrogenation of di-olefins and/or acetylenes in a hydrocarbon fraction which process comprises contacting the hydrocarbon fraction in the presence of a supported nickel catalyst comprising in addition 1 - 50 ppm by weight of a platinum group metal at a temperature in the range 0° - 250°C, a pressure in the range 7 - 100 bars gauge, a liquid hourly space velocity in the range 0.2 - 5 v/v/hr, a hydrogen treatment rate of 70 - 360 m³/m³ and a hydrogen consumption rate of 5 - 100 m³/m³.

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2. A process according to Claim 1 wherein the catalyst contains from 1 to 50% by weight of nickel.

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3. A process according to either of the preceding claims wherein the support is a refractory oxide or other refractory compound of a Group II, III or IV element.
4. A process according to Claim 3 wherein the support is sepiolite.
5. A process according to any of the preceding claims wherein the platinum group metal is palladium.
6. A process according to any of the preceding claims wherein an oxidised catalyst is reduced with hydrogen at a temperature in the range 150 to 450°C prior to selective hydrogenation.
7. A process according to any of the preceding claims wherein contacting is effected at a temperature in the range 30 - 180°C, a pressure in the range 20 - 70 bars gauge, a liquid hourly space velocity in the range 0.5 - 3, a hydrogen treatment rate of 70 - 150 m³/m³ and a hydrogen consumption rate of 10 - 90 m³/m³.
8. A process as hereinbefore described with reference to the Examples.

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Agent for the Applicants.

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